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Abstract

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STUDY OF THE CHEMICAL INTERACTION BETWEEN INDIUM AND TELLURIUM IN THE LIQUID STATE

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At present, serious attention is being devoted to questions concerning the preparation and investigation of the structure, as well as various physicochemical properties, of the compound In_2Te_3 (see (1-6), etc.). In this connection, the study of the general character and features of the chemical interaction between indium and tellurium in the molten state at various temperatures is of great interest. As is known (7), the compound In_2Te_3 melts congruently at a temperature of 667°. The crystal lattice of this compound, of the zinc-blende type, is defective with respect to the cations. The character of the bond between the atoms is homeopolar, with the presence of a comparatively small ionic component. In addition to the compound In_2Te_3, one more congruently melting compound, InTe, is formed in the indium–tellurium system; it has a complex chain structure (8).

In order to study the character of the chemical interaction between indium and tellurium in the molten state, we employed the method of physicochemical analysis, developed in the works of N. S. Kurnakov (9, 10) and associated with the construction of chemical diagrams of composition-property. Structure-sensitive properties—the viscosity and electrical conductivity of alloys of various composition—were studied over a wide temperature interval. The viscosity was determined by the Mayer-Shvidkovskii method (11, 12), and the electrical conductivity by an electrodeless method in a rotating magnetic field (13). A vacuum high-temperature apparatus was used, the design of which, as well as the working procedure, are described in detail in (14).

Indium and tellurium of purity $\sim 10^{-3} \div 10^{-4}\%$ impurities were used as starting materials for preparing the alloys. The alloys were prepared by melting the components, taken in the required amount, in quartz ampoules evacuated to 10^{-4} mm Hg and sealed.

Alloys were prepared with contents of 33; 40; 50; 51.5; 53; 55; 56; 57; 58.5; 60; 65; and 80 at. % tellurium. As a rule, measurements were carried out during heating and cooling. Alloys of different composition were, in individual cases, investigated 2–3 times and on different specimens. In some cases only heating

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

curves were recorded.

The results of the measurements are presented in the graphs (Figs. 1-3) in the form of curves of the temperature dependence of the properties studied.

Examination of the curves of the temperature dependence of viscosity (Fig. 1) shows that, according to their character, all the alloys studied can be divided into two groups.

The first group includes alloys whose compositions lie in the region corresponding to primary crystallization of the compound InTe. The temperature dependence of the viscosity of these alloys is described by smooth curves (Fig. 1a), and with increasing temperature the viscosity decreases monotonically. Such a character of the temperature dependence of viscosity is usual and is observed for most liquids.

The second group consists of alloys whose compositions lie in the region of primary crystallization of the compound In_2Te_3. The temperature depend-

the viscosity of alloys of this group is characterized by curves with a clearly expressed maximum, the maximum being most pronounced for the compound In_2Te_3 (see Fig. 16, 10). Such a character of the temperature dependence of viscosity had not been observed earlier and was first discovered by us in the study of gallium and indium tellurides and of several other compounds that in the solid state have the loose zinc-blende lattice ([15,16]).

In the study of electrical conductivity it was established that it increases noticeably with rising temperature for all alloys (see Fig. 2). The temperature dependence of the electrical conductivity of the compound In_2Te_3 was investigated

Fig. 1. Temperature dependence of the viscosity of alloys of various compositions in the indium—tellurium system. **1—12** correspond to alloys with 33; 40; 50; 53; 55; 56; 57; 58.5; 60; 65 and 80 at.% tellurium (for each alloy the upper symbol corresponds to heating, and the lower to cooling)

Fig. 2. Temperature dependence of the electrical conductivity of alloys of various compositions in the indium—tellurium system (symbols are the same as in Fig. 1)

in greater detail in the melting region and in the liquid state. The results of the measurements are given in the graph (Fig. 3). It follows from this graph

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

that in the solid state, with increasing temperature, the electrical conductivity increases exponentially. The calculation performed showed that the slope of the straight line $\lg \sigma - 1/T$ corresponds to a forbidden-band width of ~ 1 eV.

At the moment of melting the electrical conductivity increases rather sharply. Upon further heating, a sharp increase in electrical conductivity is observed in the interval $t_{\text{m}} + (50 \div 60^{\circ})$, after which the rate of increase of electrical conductivity with increasing temperature slows down, and after superheating by approximately 400° above the melting temperature the electrical conductivity of the In_2Te_3 melt practically ceases to depend on temperature. It should be noted that the described character of the change in electrical conductivity in the melting region was first observed in the work of V. P. Zhuse, V. M. Sergeeva, and A. I. Shelykh,* who studied the electrical properties of gallium and indium tellurides (^{17}). Our data for the compound In_2Te_3 agree well with the results obtained in the work of V. P. Zhuse and co-workers.

* Private communication (May 1961) and presentation at the All-Union Conference on Semiconductor Compounds in Leningrad (December 1961).

It should be noted that there is a clearly expressed correlation between the temperature dependences of the viscosity and electrical conductivity of the melt of the compound In_2Te_3. In the temperature range where the viscosity increases substantially, the electrical conductivity also rises sharply, while above the indicated temperatures a decrease in viscosity corresponds to a less noticeable increase in electrical conductivity (cf. Figs. 1b and 3).

On the basis of the results of the investigation of the temperature dependence of the properties of the alloys, chemical diagrams of viscosity—composition and electrical conductivity—composition were constructed; these are shown in Fig. 4 in comparison with the equilibrium phase diagram of indium—tellurium. It follows from this figure that the electrical-conductivity isotherms contain two clearly expressed minima. The minimum corresponding to the compound In_2Te_3 is singular. The second minimum is nonsingular and does not correspond to the compound InTe, but is shifted somewhat toward an excess of tellurium.

Fig. 3. Temperature dependence of the electrical conductivity of the compound In_2Te_3 in the solid and liquid states. Circles—on heating, triangles—on cooling

Fig. 4. Isotherms of viscosity and electrical conductivity in comparison with the equilibrium phase diagram of the state of indium—tellurium. 1—at 700°, 2—at 850°, 3—at 1000°

The viscosity isotherms are characterized by the presence of two maxima. One maximum is singular and corresponds to the compound In_2Te_3. The second maximum, in its character, is nonsingular and, like the minimum on the electrical-conductivity isotherms, is shifted somewhat relative to the ordinate of the InTe compounds toward an excess of tellurium. The observed character of the viscosity and electrical-conductivity isotherms makes it possible to conclude that the compound In_2Te_3 is very stable after melting in the liquid state and only after considerable superheating, apparently, partially dissociates, as evidenced by the blurring of the extrema on the composition—property diagrams.

The compound InTe, judging from the character of the isotherms of the properties investigated, partially dissociates directly at the melting temperature. A viscosity maximum analogous to that obtained in the present work was observed in the works of N. S. Kurnakov and N. N. Efremov, and also of N. S. Kurnakov and N. I. Podkopaev, using the examples of the systems water—bromal ([18]) and water—sulfuric anhydride ([19]). On the basis of the character of the viscosity and electrical-conductivity isotherms, as well as the character of the temperature dependence of the investigated properties, it may be assumed that upon melting of the compound In_2Te_3 the homeopolar bond between atoms is preserved.

An increase in viscosity and electrical conductivity within the narrow temperature interval
$t^\circ_\mathrm{m} + (50 \div 60^\circ)$ after melting of the compound In_2Te_3 can be associated with changes in the short-range-order structure in the direction of an arrangement of the structural units of the melt according to the principle of close packing, taking into account the nature of the symmetry of these structural units and the interaction between them.

Attention is drawn to the presence of a deep minimum in the concentration range between the compounds InTe and In_2Te_3, which corresponds to the eutectic concentration. The coincidence of the viscosity minimum with the eutectic, in the presence of a symmetrically convex character of the liquidus curves, is possible when there is a developed chemical microinhomogeneity of the melt, which indicates weak interaction between particles of different kinds (20). Obviously, in the present case, since the compound InTe dissociates, the presence of the minimum can be explained by the weak interaction of the compound In_2Te_3 with the dissociation products formed during melting of the compound InTe, which emphasizes the special features of the compound In_2Te_3 as a chemical individual in the liquid state.

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Note: Figure translations are in progress. See original paper for figures.